PHYSICAL REVIEW VOLUME 162, NUMBER 3 15 OCTOBER 1967

Lattice Thermal Conductivity of Solid Helium. II. Isotopic Mixtures

BAL KRISHNA AGRAWAL
Physics Department, Allahabad University, Allahabad, India

(Received 23 February 1967)

We have analyzed the thermal-conductivity data of He^4-rich isotopic mixtures of solid helium in the hcp phase and He^3-rich mixtures in the bcc phase at the molar volume 20.2 cm^3/mole measured by Bertman *et al.* It is found that the T^3 dependence of normal processes generally used in Callaway's model can explain the thermal-conductivity data in the temperature range 0.6 to 1.8°K. The concentration dependence of the lattice distortion scattering due to added isotopic impurity is seen to be the theoretically expected one, i.e., $x(1-x)$, and the stronger concentration dependence noticed by Bertman is not observed.

INTRODUCTION

SEVERAL attempts[1-4] have been made to understand the variation of thermal conductivity of isotopic mixtures of solid helium with the concentration of the added isotopic impurity at different densities or pressures. Recently two groups of workers, Berman *et al.*[3] and Bertman, *et al.*,[4] have drawn different conclusions regarding the intrinsic lattice distortion scattering due to added isotopic impurities. The Rayleigh-type phonon scattering due to an impurity in a solid may be expressed as $\tau_{pt}^{-1}=A\omega^4$, where τ_{pt} is the relaxation time for the phonon of frequency ω, and A determines the strength of the scattering. According to Klemens,[5] A can be expressed as $A=A_{\text{mass}}+A_{\text{lattice}}$, where A_{mass} refers to scattering due to mass fluctuations. For He^3-He^4 mixtures, the concentration dependence of A_{mass} is given by $x(1-x)$, where x represents the fraction of the added isotopic impurity. A_{lattice} refers to scattering of phonons by the lattice distortion around the impurity and is of much importance for solid helium which has a large zero-point energy. The substitution of one isotope for another causes a large distortion in the lattice.

Berman *et al.* assumed that the relaxation rate for three-phonon normal processes is proportional to ω^2T^2, and they determined the strength of the isotopic impurity scattering A from their experimental data. They found that the ratio A/A_{mass} remains constant as the composition of He^3-He^4 mixtures at a given pressure of formation is varied. Since $A_{\text{mass}}\propto x(1-x)$, it may be concluded that the concentration dependence of A_{lattice} is also given by $x(1-x)$. Bertman *et al.*[4] have also obtained the same concentration dependence from theoretical considerations. However, Berman *et al.*'s values[3] of A at various pressures of formation of solid mixtures were considerably less than had been calculated on the basis of the rough estimate given earlier by Klemens and Maradudin.[6] On the other hand, Bertman *et al.* assumed the ω^2T^3 dependence of the normal processes in analyzing their experimental data, and obtained much higher values of A than those obtained by Berman *et al.* The observed intrinsic strength of the lattice-distortion scattering depended on concentration more strongly than the expected $x(1-x)$.

The essential difference between the two analyses lies only in the treatment of the normal processes, and the observed large difference in the nature of the determined values of A was not understandable. To gain a better understanding, it was considered worthwhile to analyze in detail the thermal-conductivity data of isotopic mixtures of solid helium at some other density. Thus we have analyzed the experimental data of Bertman *et al.* at the molar volume 20.2 cm^3/mole. At this molar volume, pure solid He^4 exists in hexagonal close-packed structure, while pure solid He^3 crystallizes in the body-centered-cubic structure. It is interesting to note that the values of the Debye temperature Θ is practically the same (27°K) for the two isotopes at this particular molar volume 20.2 cm^3/mole. We have used Callaway's theory to analyze the thermal-conductivity data of He^4-rich mixtures in the hcp phase and He^3-rich mixtures in the bcc phase by using the T^3 dependence of three-phonon normal processes, and we have obtained some decisive results.

DATA ANALYSIS

The thermal conductivity according to Callaway is given by[7,8]

$$K=\left(\frac{k}{2\pi^2c}\right)\left(\frac{kT}{h}\right)^3[I_1+\beta I_2],$$

where

$$I_1=\int_0^{\Theta/T}\tau_C\frac{e^x}{(e^x-1)^2}x^4dx,$$

$$I_2=\int_0^{\Theta/T}\frac{\tau_C}{\tau_N}\frac{e^x}{(e^x-1)^2}x^4dx,$$

---

[1] E. J. Walker and H. A. Fairbank, Phys. Rev. **118**, 913 (1960).

[2] J. Callaway, Phys. Rev. **122**, 787 (1961).

[3] R. Berman, C. L. Bounds, and S. J. Rogers, Proc. Roy. Soc. (London) **A289**, 66 (1965).

[4] B. Bertman, H. A. Fairbank, R. A. Guyer, and C. W. White, Phys. Rev. **142**, 79 (1966).

[5] P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951).

[6] P. G. Klemens and A. A. Maradudin, Phys. Rev. **123**, 804 (1961).

[7] J. Callaway, Phys. Rev. **113**, 1046 (1959).

[8] The term βI_2, which is usually negligible, makes a major contribution in the case of pure solid helium as shown in a previous paper [Bal Krishna Agrawal and G. S. Verma, Phys. Rev. **128**, 603 (1962)].

and

$$\beta=I_2\Big/\int_0^{\Theta/T}\frac{1}{\tau_N}\left(1-\frac{\tau_C}{\tau_N}\right)\frac{e^x}{(e^x-1)^2}x^4dx\,;$$

k is Boltzmann's constant and $x=\hbar\omega/kT$. The combined relaxation time τ_C is given by

$$\tau_C^{-1}=\tau_B^{-1}+\tau_{pt}^{-1}+\tau_N^{-1}+\tau_U^{-1},$$

and the various relaxation times are as follows:

boundary scattering: $\tau_B^{-1}=c/L$,
impurity scattering: $\tau_{pt}^{-1}=A\omega^4$,
normal processes: $\tau_N^{-1}=B_NT^3\omega^2$,
umklapp processes: $\tau_U^{-1}=B_UT^3\omega^2e^{-a/T}$,

where c is the mean sound velocity, Θ is the Debye temperature, L is the diameter of the cylindrical sample, and a is a parameter depending upon the crystal structure of the solid.

Recently, Guyer and Krumhansl,[9] by solving the linearized phonon Boltzmann equation, have studied in detail the role played by three-phonon normal processes in determining the thermal conductivity of solids. They have developed an alternative to Callaway's equation. [See Eq. (44) of Reference 8]. It has been stated that their equation for thermal conductivity can be derived from the Callaway equation if the matrix elements of products of relaxation times are replaced by the product of the matrix elements subject to the identification of the collision operators with the relaxation rates. When the normal processes are too rapid compared to all other scattering processes, e.g., umklapp scattering, mass-fluctuation scattering, etc., the results reduce to the Ziman limit in which thermal resistivities can be added. For normal processes much slower than other scattering processes, the relaxation-time approximation is obtained.

The thermal conductivity in the Ziman limit,[10] after considering the mass-fluctuation scattering, is given by

$$K=[\hbar/120\pi^2cA_{\text{mass}}T][1/x(1-x)],$$

where A_{mass} is the Klemans mass-fluctuation scattering given by[5]

$$A_{\text{mass}}=(V/4\pi Nc^3)(\Delta m/\bar{m})^2.$$

Here N is Avogadro's number, and Δm and $\bar{m}$ denote the mass difference of isotopes and the average isotopic mass, respectively. To see the validity of the approximation, we have calculated the values of thermal conductivity in the temperature range 0.5 to 1°K for the two observed concentrations $x=0.0089$ and $x=0.097$ of He^3 in He^4 mixtures. The values are shown in Fig. 1 by dotted lines. We make two observations from these curves. Firstly, at $x=0.0089$, the calculated values of conductivity in the Ziman limit are higher than the experimentally measured values. This result predicts the presence of some stronger scattering mechanism than the mass-fluctuation scattering. It may arise because of lattice distortion. Secondly, at $x=0.097$, the the values in the Ziman limit are lower than the experimental ones. This result invalidates the additive resistivity approximation. Here normal processes are too slow compared with other scattering mechanisms and are unable to transfer momentum from weak scattered states to strong scattered states. The various groups of phonons lose momentum individually and the relaxation rates are different for different states. The relaxation-time approximation is true in these circumstances.

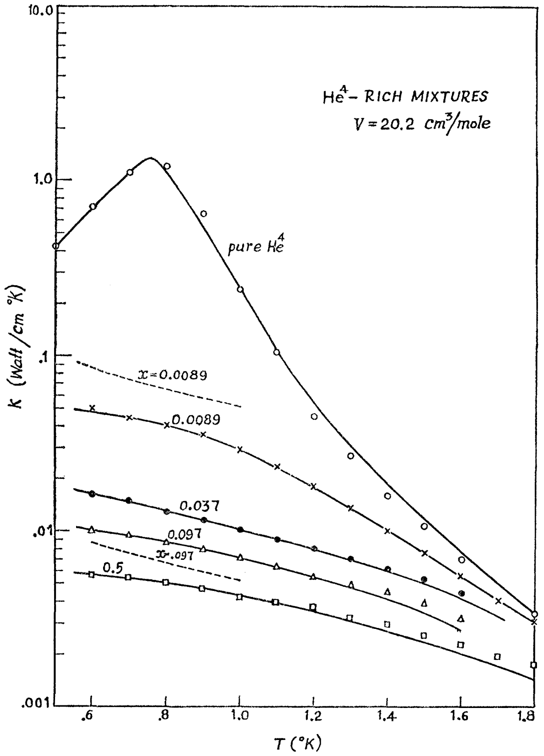

FIG. 1. Variation of thermal conductivity of solid He^4-rich mxtures at different concentrations in the hcp phase at the molar volume 20.2 cm^3/mole. Continuous curves represent the calculated values. Experimental values are denoted by points of different shapes. The values of thermal conductivity in the Ziman limit at concentrations $x=0.0089$ and 0.097 of He^3 are represented by dashed lines.

The gross features of the curves showing thermal conductivities at different temperatures for He^4-rich mixtures at molar volume 20.2 cm^3/mole are very similar to the curves at molar volume 19.5 cm^3/mole. At both densities, He^4-rich mixtures exist in hexagonal close-packed crystal structures. But the behavior of solid He^3 is different. At the molar volume 19.5 cm^3/mole, all the He^3-rich mixtures exist in the hcp structure, but at 20.2 cm^3/mole, pure He^3 exists in the body-centered-cubic crystal structure. For not very high concentrations of added He^4 atoms, He^3-rich mixtures

---

[9] R. A. Guyer and J. A. Krumhansl, Phys. Rev. 148, 766 (1966).
[10] J. M. Ziman, Can. J. Phys. 34, 1256 (1956).

are not expected to change their bcc structures. The values of thermal conductivity of solid He^3 in the bcc phase are in general much smaller.

In the Callaway model the phonon spectrum of the solid is taken on the basis of Debye model, and thus it is advisable to keep the characteristic Debye temperature constant among the different isotopic compositions of solid helium. Berman *et al.* had assumed that values of Θ were probably very similar for solids formed at the same pressure regardless of the isotopic constitution; therefore they measured the conductivities of the solids while keeping constant the pressure of formation, rather than the pressure in the resulting solid or the density. Bertman *et al.* have performed measurements at constant density or molar volume. At the molar volume 19.5 cm^3/mole, the Debye temperatures for pure solid He^4 and He^3 were 30 and 34.6K, respectively. Hence the values of Θ for the composite solid were likely to vary with the concentration of the added isotope. But at molar volume 20.2 cm^3/mole, the values of the Debye temperature for pure solid He^4 and He^3 are practically the same, i.e., 27°K as a result of the phase transformation of He from the hcp structure of He^4 to the bcc structure of He^3. Therefore the problem of the altered value of Θ is not expected to arise for the solids of isotope mixtures at the considered molar volume 20.2 cm^3/mole.

The values of the Debye temperature for pure He^4 and He^3 were taken from the results of Heltems and Swenson.[11] Recent values determined by Edward and Pandorf[12] for the case of solid He^4 are practically the same. Knowing Θ, the velocity of sound waves c was determined by the relation $c=(k\Theta/\hbar)\,(V/6\pi^2N)^{1/3}$ and was seen to be 2.9×10^4 cm/sec. Using this value of sound velocity, the reciprocal of the boundary relaxation time τ_B^{-1} was found to be 1.46×10^5/sec. The value of c/L required to explain the data on pure He^4 and He^3 at the lowest temperature 0.5°K., where all other scattering mechanisms were negligible except the boundary scattering, was seen to be 7.2×10^6 sec^{-1}. This experimentally determined value for boundary scattering was five times larger than the value obtained by the Casimir theory. This may be due to the presence of a few large crystals rather than a single crystal formed by the block capillary technique as suggested by Bertman.[13]

Using this experimentally determined value for boundary scattering, the thermal-conductivity curves of pure He^4 and He^3 were explained by varying the values of the parameters B_N, B_U, and a. It was observed that a number of the values of the parameters of the set (B_N,B_U,a) were able to fit the data on pure He^4 or He^3. No unique set of values for the parameters (B_N, B_U, and a) was obtained to explain this data. Therefore for each value of B_N, values of B_U and a were determined to fit the data. In analyzing the data, we observe that the βI_2 term of the Callaway equation makes a major contribution the total thermal conductivity at all temperatures except above 1.4°K, where umklapp processes are dominant. This will be the case whenever normal three-phonon processes are very rapid compared to other scattering mechanisms such as boundary scattering and umklapp processes. The additive resistivity approximation is valid in these circumstances, i.e., for the data on pure He^3 or He^4 below 1.4°K.

To account for the measured difference between the conductivities of pure solid helium and of a mixture, it is assumed that the two solids are sufficiently similar for the relaxation rates for scattering by intrinsic three-phonon processes to be taken as the same. Therefore the values of c/L, B_N, B_U, and a determined in the case of the He^4 and He^3 pure data are not expected to change in the mixed solids and are used in the analysis of the composite solids. The values of the parameters A and B_N are varied over a large range to determine a good fit to the thermal-conductivity curves of mixture solids in the temperature range 0.6 to 1.4°K. As mentioned earlier, in this low-temperature range the umklapp processes are not dominant, and the values of A and B_N could be determined unambiguously to better than 10% for the majority of concentrations and to 15% for a few concentrations. The computed curves are compared with the experimental values of thermal con-

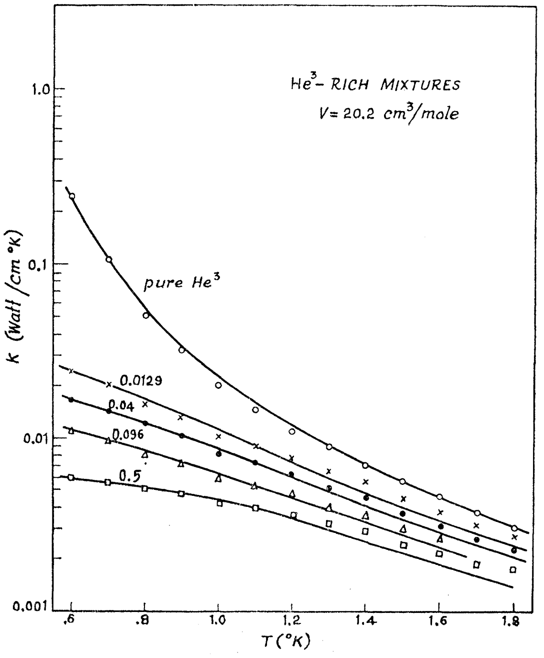

FIG. 2. Variation of thermal conductivity of solid He^3-rich mixtures at different concentrations in the bcc phase at the molar volume 20.2 cm^3/mole. Continuous curves represent the calculated values. Points of different shapes denote the experimental values.

---

[11] E. C. Heltemes and C. A. Swenson, Phys. Rev. **128**, 1512 (1962).

[12] D. O. Edwards and R. C. Pandorf, Phys. Rev. **140**, 816 (1965).

[13] B. Bertman, H. A. Fairbank, C. W. White, and M. J. Crooks, Phys. Rev. **142**, 74 (1966).

TABLE I. Values of the parameters (A, B_N, B_U, and a) and the ratios $A/x(1-x)$ and A/A_{mass} for He^4-rich mixtures in the hcp phase.

Concentration of He^3 x	A (10^{-39} sec^3)	B_N (10^{-16} sec deg^{-4})	B_U (10^{-13} sec deg^{-4})	a (deg)	$\frac{A}{x(1-x)}$ (10^{-36} sec^3)	A_{mass} (10^{-39} sec^3)	A/A_{mass}
0	...	1.0	1.3	9	...	...	...
0.0089	1.74	1.5	1.2	9	0.20	0.059	30
0.037	7.60	4.0	1.3	9.5	0.21	0.24	32
0.097	22.4	4.5	1.3	9.5	0.28	0.64	35
0.50	55.2	5.0	1.2	9.5	0.22	2.06	27

TABLE II. Values of the parameters (A, B_N, B_U, and a) and the ratios $A/x(1-x)$ and A/A_K for He^3-rich mixtures in the bcc phase.

Concentration of He^4 x	A (10^{-39} sec^3)	B_N (10^{-16} sec deg^{-4})	B_U (10^{-15} sec deg^{-4})	a (deg)	$\frac{A}{x(1-x)}$ (10^{-36} sec^3)	A_{mass} (10^{-29} sec^3)	A/A_{mass}
0	...	3	4.5	3	...	...	...
0.0129	3.6	3	4.5	3	0.28	0.15	24
0.04	10.2	3	4.5	3	0.27	0.44	23
0.096	20.4	3	4.5	3	0.24	0.97	21
0.50	51.1	3	4.5	3	0.21	2.06	24

ductivity in Figs. 1 and 2. The values of the parameters taken in the calculations are shown in Tables I and II. To display the concentration dependence of A, values of $A/x(1-x)$ have been given in these tables. Further, the values of A/A_{mass} are also given to determine the strength of the total impurity scattering.

He^4 in the hcp Phase

Solid He^4 in the hexagonal close-packed crystal structure at various densities has been analyzed by a number of workers. The two recent analyses of Berman *et al.*[3] and Bertman *et al.*[4] have led to different results. Bertman *et al.*, taking the normal processes as proportional to ω^2T^3, concluded that the strength of the intrinsic lattice distortion scattering depended on concentration more strongly than the theoretically expected one, i.e., $x(1-x)$. The present analysis of the data of He^4-rich mixtures at the molar valume 20.2 cm^3/mole has been performed by assuming the T^3 dependence of normal processes. From Table I, we see that the determined values of A are high and the values of $A/x(1-x)$ and A/A_{mass} are more or less similar. It means that the concentration dependence of lattice distortion scattering is $x(1-x)$, as expected by analogy to mass fluctuation scattering. The possibility of the presence of stronger concentration dependence is not seen in the analysis of data at the molar volume 20.2 cm^3/mole. To have a clear picture we have compared the values of $A/x(1-x)$ obtained by Bertman and the present analysis in Table III.

The second analysis given by Berman *et al.* uses the T^2 dependence of normal processes. The conclusions drawn from their analysis are similar to the present results with regard to the concentration dependence of lattice distortion scattering. The validity of their choice of a T^2 dependence for normal processes is not clear, as it is considered more appropriate for higher temperatures. Recently, Guyer and Krumhansl[14] have utilized Poiseulle flow (i.e., very high thermal conductivity of large crystals below the conductivity maximum, observed by Mezov-Deglin[15] in pure He^4) for the calculation of the relaxation time of normal processes in the low-temperature range 0.5°K to 0.8°K. They considered that these values of τ_N were more directly measured, and showed that these values are in close agreement with the values of τ_N used by Bertman *et al.* in the analysis of their thermal-conductivity data. The values of τ_N found by Berman *et al.* were seen to be 10 to 20 times smaller than these directly determined values of τ_N. The value of B_N in the present analysis is similar to Bertman's value and therefore our values of τ_N are similar to his. Table IV contains the values of τ_N at different temperatures.

However, the results of Berman *et al.* do not predict

TABLE III. Normal process relaxation times for pure solid He^4. Values of columns (a), (b), and (c) are at 19.5 cm^3/mole and are quoted from Guyer and Krumhansl (Ref. 13). Column (d) contains values at the molar volume 20.2 cm^3/mole.

T(°K)	(a) Mezhov-Deglin (μsec)	(b) Bertman *et al.* (μsec)	(c) Berman *et al.* (μsec)	(d) Present calculations (μsec)
0.5	1.0	1.2	0.05	1.2
0.6	0.7	0.5	0.02	0.5
0.7	0.4	0.2	0.01	0.2
0.8	0.3	0.1	0.007	0.1
0.9	...	0.06	0.004	0.06

---

[14] R. A. Guyer and J. A. Krumhansl, Phys. Rev. **148**, 778 (1966).

[15] L. P. Mezhov-Deglin, Zh. Eksperim. i Teor. Fiz. **49**, 66 (1965) [English transl.: Soviet Phys.—JETP **22**, 47 (1966)].

TABLE IV. Comparison of the values of $A/x(1-x)$ at the two molar volumes 19.5 cm^3/mole and 20.2 cm^3/mole of the He^3-He^4 mixtures.

	Concentration (x)	Bertman (Ref. 4) values at 19.5 cm^3/mole (10^{38} sec^3)	Present values at 20.2 cm^3/mole (10^{38} sec^3)
He^4-rich mixtures	0.0089	9.7	20
	0.038	12.3	...
	0.037	...	21
	0.097	18.3	28
	0.50	13.2	22
He^3-rich mixtures	0.0129	4.88	28
	0.04	6.5	27
	0.096	11.5	24
	0.50	13.2	21

the presence of excess lattice distortion scattering over the expected one, a conclusion similar to ours. Their values of A were low and were approximately seven times smaller than the theoretically determined values of strain field scattering based on Klemens's rough estimate.[6,16] The numerical estimate of Klemens has a large uncertainty due to various approximations involved in the derivation. Berman *et al.* considered the thermal conductivity data in the higher temperature range 1.2–2°K, where umklapp processes make an appreciable contribution to thermal conductivity. In the present paper the measurements of Bertman *et al.* are analyzed to still lower temperatures, i.e., to 0.6°K, where umklapp processes are not dominant and thus allow us to choose more decisive values of A and B_N. Our analysis gives higher values of A as may be seen from Table I.

Klemens and Maradudin have considered scattering due to distorted lattice around the impurity as Rayleigh-type and shown that the relaxation time for lattice distortion scattering may be represented by

$$\tau_{\text{lattice}}^{-1}=(V/4\pi Nc^3)\times 140\gamma^2\epsilon^2\omega^4=A_{\text{lattice}}\omega^4\,,$$

where $\gamma=\delta R/R$ is the Gruneisen constant denoting the atomic misfit of an atom in the host lattice. To estimate ϵ, we take[2,17] $\gamma=2.6$ and use the average value of $A_{\text{lattice}}/x(1-x)$. The value of ϵ is seen to be $\simeq$4.5%, a value slightly higher than that of Bertman *et al.*

He^3 in the bcc Phase

The values of thermal conductivity of solid helium having the bcc crystal structure are seen to be much lower than the values in the hcp phase. This anomalous decrease of conductivity in the bcc phase is difficult to understand. Few attempts have been made to explain the thermal conductivity in the bcc phase. To explain the data of pure He^3 in the bcc phase Bertman *et al.*[13] assumed the presence of two competing umklapp phonon-scattering mechanisms having different excitation energies. For determining total resistance, the thermal resistivities due to the two umklapp processes were added. In addition to the above anomalous behavior there still existed a slight dip in the thermal conductivity curves centered around 1°K and the possibility of a resonance-phonon-scattering mechanism was suggested.

The thermal-conductivity curves of solid He^3 in the bcc phase at the molar volume 20.2 cm^3/mole are explained and the results are shown in the Fig. 2. We note that the dips appear near 1°K in all its mixtures. In pure solid He^3, the only point defects present are lattice vacancies which might be responsible for the occurrence of resonance scattering of phonons. The fact that dips occur near 1°K in all the mixture solids suggests that the vacancies of the pure solid responsible for resonance scattering exist in them. The possibility of the resonance scattering of phonons by the lattice vacancies, if they are in sufficiently large number, has been demonstrated by Shwartz and Walker.[18] It seems that such a situation exists in pure He^3 and its mixtures. But the dips are not much pronounced and we assume that the magnitude of the resonance scattering required to explain these small dips do not affect our determined values of A appreciably.

The values of the various parameters used in the calculations are shown in Table II. We see from the table that the value of a in the exponential dependence of umklapp processes is extraordinarily low. Further, only one set of values for the parameters (B_N, B_U, and a) is able to explain the data at different concentrations of He^4 in He^3. The magnitude of umklapp processes is high because of the large value of a and is unlikely to show a visible change when the concentration of the added isotopic impurity is varied.

From Fig. 2, it is seen that the computed curves are in reasonably good agreement with the experimental values at all concentrations except at 50% He^4 in He^3. At 50% concentration, the poor fit at temperatures higher than 1.3°K may be attributed to the uncertainty involved in choosing the exponential dependence of umklapp processes. The crystal structure at this concentration is not known. A better fit may be obtained for the hcp phase of this concentration. When one compares the values of thermal conductivity observed in the case of 50% He^3 in He^4 with the values of the solid having 50% He^4 in He^3, one hardly observes any difference except at very low temperatures below 0.7°K. Thus there may be a possibility of phase transformation from the bcc phase to the hcp phase.

Again the values of $A/x(1-x)$ are similar for different concentrations, as are the values of the ratios A/A_K, an observation similar to the case of He^4-rich mixtures in the hcp phase. The value of the atomic misfit parameter ϵ comes out to be $\simeq$4.7%, which is very near

---

[16] P. G. Klemens, de Bruyn Ouboter, and R. Pair, Physica **30**, 1863 (1964).

[17] D. O. Edwards and R. C. Pandorf, Phys. Rev. **144**, 143 (1966).

[18] J. W. Schwartz and C. T. Walker, Phys. Rev. Letters **16**, 97 (1966).

TABLE V. Experimental and theoretical values for the ratio A/A_{mass} obtained by various workers.

	Filling pressure (atm)	Molar Volume (cm^3/mole)	$A_{\text{exp}}/A_{\text{mass}}$	$A^{a}{}_{\text{cal}}/A_{\text{mass}}$ [e]
He^4-rich mixtures	60[a]	...	2.8	10
	90[a]	...	2.0	8.3
	140[a]	...	1.5	5.6
	96[b]	...	$\sim$3	...
	...	19.5[c]	21–41	...
	...	20.2[d]	$\sim$31	...
He^3-rich mixtures	145[a]	...	1.2	2.8
	...	19.5[c]	9–27	...
	...	20.2[d]	$\sim$23	...

[a] Values of Berman *et. al.* (Ref. 3).
[b] Values of Callaway (Ref. 2).
[c] Values of Bertman *et al.* (Ref. 4).
[d] Present values.
[e] Reference 5, 6.

the value observed in the hcp phase of solid He^4. Finally, in Table V, we have summarized all the known experimental and theoretical values of A/A_{mass}.

CONCLUSIONS

The thermal-conductivity curves of isotopic mixtures of solid He^4 have been analyzed at the molar volume 20.2 cm^3/mole. The He^4-rich mixture solids at this molar volume have the hcp crystal structure while the He^3-rich mixtures crystallize in the body-centered-cubic structure. The Debye temperatures are similar in the case of pure He^4 and pure He^3, thus diminishing the possibility of the variation of sound velocity in the mixed solids.

Large values of phonon scattering by point defects are obtained from the analysis. The enhanced scattering is considered to be present because of the distortion of the lattice around the isotopic impurity. The concentration dependence of phonon scattering produced by lattice distortion is found to be the theoretically expected one. These conclusions are different from the earlier conclusions of Bertman *et al.* The magnitudes of the lattice distortion scattering are also higher than the values obtained by Berman *et al.* The estimates of the atomic misfit parameter ϵ are the same in both phases of solid helium.

ACKNOWLEDGMENTS

The author expresses his gratitude and sincere thanks to Professor G. S. Verma for his helpful suggestions and discussion.

PHYSICAL REVIEW VOLUME 162, NUMBER 3 15 OCTOBER 1967

Electronic Structure of the *U* Center. I. Optical Absorption and Lattice Relaxation*

R. F. WOOD
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee
AND
U. ÖPIK
Department of Applied Mathematics, The Queen's University, Belfast, Northern Ireland

(Received 7 June 1967)

The electronic structure of the *U* center in KCl, KBr, and KI is calculated for the ground and first excited states using a model in which the interactions with the first-nearest-neighbor ions are taken into account in detail and all other ions are treated as point charges. A second, more refined model, which involves the electronic structure of all ions and polarization effects, is briefly described. It is used for calculations of the electronic structure, optical absorption, and lattice relaxation of the *U* center in KCl.

I. INTRODUCTION

THE *U* center in alkali-halide crystals consists of an H$^-$ ion trapped at a lattice site normally occupied by a negative halogen ion. The center has been studied extensively experimentally, and several interesting properties have been established.[1] It is responsible for a single pronounced characteristic absorption in the ultraviolet (at approximately 5.8 eV in KCl). Other absorption bands are probably associated with the center, but, if so, they are difficult to observe because of masking by the intrinsic absorption of the pure crystals. In contrast to many other defects in alkali-halide crystals, no emission bands have been associated with the *U* center. Instead, a number of photochemical reactions take place, which suggests that in the excited state of the center the neutral hydrogen atom is able to diffuse away from the vacancy into an interstitial position. The result is that the *U* band is bleached and the *F* band is generated. The diffusion process should be aided by lattice relaxation if in the relaxed state the excited electron is in a diffuse orbital, as might be expected from results on the *F* center.[2,3]

---

* Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

[1] J. H. Schulman and W. Dale Compton, *Color Centers in Solids* (Pergamon Press, Inc., New York, 1962).

[2] W. B. Fowler, Phys. Rev. **135**, A1725 (1964).

[3] R. F. Wood and H. W. Joy, Phys. Rev. **136**, A451 (1964).